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Heterogeneous catalysts for the production of anthraquinone from 2-benzoylbenzoic acid

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Abstract

In the present paper, the dehydration reaction of 2-benzoylbenzoic acid (BBA) has been investigated in the presence of different heterogeneous catalysts, based on heteropoly acids (polyoxometalates), by using, in a first approach, a batch reactor for screening the best catalysts and, in a second step, a pseudo-continuous multifunctional reactor for determining reaction yields, catalysts productivity and deactivation of the catalyst selected in the first part of the research.

The pseudo-continuous reactor works also as evaporator and condenser for separating and collecting produced anthraquinone (AQ) at a high level of purity, while water continuously evaporates in the atmosphere.

A productivity comparison has also been reported with respect to solid acid catalysts, i.e. Y and β zeolites and acidified bentonite, tested previously.

A kinetic model with vapour–liquid partition, liquid-phase non-ideality and catalyst deactivation, has been developed to correlate the experimental runs.

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Keywords: Anthraquinone production; 2-Benzoylbenzoic acid reagent; Acid catalysts; Polyoxometalates; Multifunctional reactor

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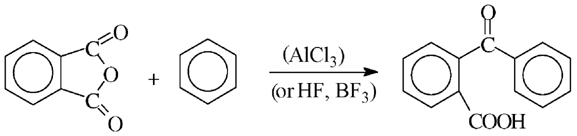
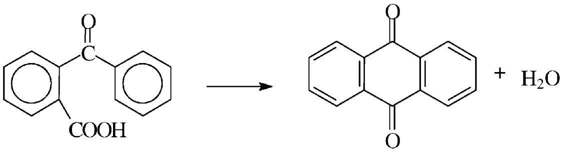
1. Introduction

Previously some solid acid catalysts have been tested in the reaction of dehydration of 2-benzoylbenzoic acid (BBA) for producing anthraquinone (AQ) [1]. In the past, the most common method for the manufacture of AQ was the oxidation of anthracene by different oxidants acting in gas or in liquid phase [2]. As, the availability of anthracene is declining, alternative processes have been developed and among them an interesting route starts from benzene and phthalic anhydride [2]. This synthesis consists of two reaction steps



(1)



(2)

The first step has been studied in the presence of HBF$_4$ [3] as well as in the presence of AlCl$_3$ [4]. The second step is the cyclization via dehydration of BBA, and is commonly promoted by concentrated H$_2$SO$_4$, that is used also as a solvent [5,6]. Many other catalysts have been proposed in the literature such as: phosphoric acid [7], silica–alumina [8], acid clays [1,9,10], zeolites [1,11,12] and perfluoro acid resins [13]. The reaction is normally performed by contacting the solid catalyst with the molten reactant or with a solution of the reagent in an appropriate solvent at temperatures favouring the vaporisation of the water formed in the reaction.

In the present paper, BBA dehydration has been studied in the presence of different polyoxometalate catalysts with strong acid character, using both a batch and a pseudo-continuous reactor. Batch runs have been performed for screening the catalysts, while, the continuous reactor was used with the best catalyst to obtain detailed information regarding kinetics, catalyst productivity, reaction yields and catalyst deactivation.

The continuous reactor employed is a multifunctional reactor developed in our previous work [1], operating also as a separation unit for collecting, by evaporation, produced AQ at a high level of purity. In the meantime, water formed continuously evaporates in the atmosphere.

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Nomenclature

J	total molar flow rate
J_{AQ}	anthraquinone molar flow rate
J_{H_2O}	water molar flow rate
k_c	kinetic constant
k_0	initial kinetic constant
k_d	deactivation constant
m	mass of catalyst
n_{BBA}	moles of benzoyl-benzoic acid
n_{BBA}^0	initial moles of benzoyl-benzoic acid
n_{AQ}	moles of anthraquinone
n_{AQ}^L	moles of anthraquinone in the liquid phase
n_{AQ}^S	moles of anthraquinone collected as solid
n_{H_2O}	moles of water
P	total pressure
P_{AQ}^0	anthraquinone vapour pressure
r	reaction rate
t	time
x_{AQ}	anthraquinone liquid mole fraction
γ_{AQ}	anthraquinone liquid activity coefficient
y_{AQ}	anthraquinone vapour mole fraction

We have found that a synthesised polyoxometalate catalysts, $H_7PW_{12}O_{42}\cdot xH_2O$, gives much better performances than those achieved with previously tested catalysts such as acid bentonites and Y and β zeolite [1].

A kinetic model with non-ideal vapour–liquid partition, also considering catalysts deactivation, developed in a previous work [1], has been used for simulating the pseudo-continuous runs and the related parameters have been estimated.

A comparison of the different catalysts performances will conclude the paper.

2. Experimental: methods, apparatus and reagents

Catalytic screening has been made in a 250 cm^3 round bottom flask of glass, about 4 g of BBA (FLUKA) were put in the flask together with an amount of the solid catalyst that corresponds to a molar ratio BBA/catalyst of 1000. Then, the flask was dipped for 2 h in a thermostatted oil bath, kept at 200 °C, stirring the molten reaction mixture with a magnetic stirrer. After 2 h of reaction, conducted on the molten reactant, the flask was cooled and the reaction mixture was treated with a first solvent (dichloromethane), dissolving both AQ and BBA and separating them from the catalyst. The solvent is evaporated and the product mixture was then submitted to chemical analysis as follows. A weighed amount of the mixture was further dissolved in 20 cm^3 of methanol and titrated with NaOH 0.1 M. In this way, the residual mass of BBA in the mixture was determined. AQ formed was determined by difference.

The employed catalysts are listed in Tables 1 and 2, together with the adopted operative conditions. In this table are also listed the literature references for the synthesis of heteropolyacids in which can be found detailed description of preparation procedure. In this table is also reported the result of a blank experiment on alumina.

All the catalysts are solid polyoxometalates with high acid character; one of them is a commercial product (FLUKA) and the others have been synthesised by adopting the literature procedures.

Continuous runs have been performed in the reactor/evaporator schematised in Fig. 1. Three zones in this reactor are working at different temperatures: (i) the reacting zone in which the reagent and catalyst are initially loaded and are kept at the reaction temperature (240 or 300 °C) with a furnace, (ii) the neck heated at temperatures of about 340 °C to favour the diffusion of the vapours of AQ and water, (iii) the product recovering zone that is cooled with a cold air stream in which the sublimated AQ crystallises.

At the top of the reactor a hole in the cover allows the evacuation of the vaporised water. AQ is manually withdrawn from the lateral tube reported in the scheme having at the extremity a stopper. The amounts of AQ, withdrawn at regular intervals of time during the reaction, were replaced by an equivalent molar amount of fresh reagent introduced from another hole on the cover that is normally kept closed with a stopper. The molten reacting mixture is magnetically stirred.

Table 1
Results for batch runs with polyoxometalate catalysts

Polyoxometalate catalysts	Reference for synthesis	Ratio BBA/catalyst (mol/mol)	Yield (mol% of anthraquinone) $(n_{AQ}/n_{BBA}^0)100$
$H_3PW_{12}O_{40}$ (commercial[a])	–	1000	20.9
$H_7PW_{12}O_{42}$ hydrate	[15]	1000	28.5
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	[16]	1000	22.2
$H_4SiW_{12}O_{40}$ hydrate	[15]	1000	16.4
$(NH_4)_3PW_{12}O_{40}$ hydrate	[17]	1000	21.5
$H_3PMo_{12}O_{40}$ $14H_2O$	[19]	1000	18.7
$H_4SiMo_{12}O_{40}$ hydrate	[15]	1000	12.6
$H_3PMo_{10}V_2O_{40}$	[18]	1000	13.8
Alumina (blank experiment)	–	1000	0.05

AQ: anthraquinone; BBA: 2-benzoylbenzoic acid.

[a] Fluka.

Table 2
Results for pseudo-continuous runs, comparison of maximum overall productivity

Catalyst	Temperature (°C)	Molar or weight ratio BBA/catalyst	Maximum overall productivity (g AQ/h/g catalyst)
$H_7PW_{12}O_{42}$ hydrate	240	100[a]	0.0486↔
$H_7PW_{12}O_{42}$ hydrate	300	100[a]	1.414↔
Bentonite F21-B	290	0.49[b]	0.0381↓
Bentonite F21-B regenerated	290	0.49[b]	0.0656↓
Y zeolite	290	0.50[b]	0.0494↓
Y zeolite regenerated	290	0.50[b]	0.1146↓
β zeolite	290	0.50[b]	0.0565↓
β zeolite regenerated	290	0.41[b]	0.0901↓

The symbol (↓) indicates: the productivity decrease, more or less steeply, after reaching the maximum, for the catalyst deactivation. The symbol (↔) indicates: a quite stable trend in productivity is obtained after about 400 min of reaction time.

[a] Molar ratio.

[b] Weight ratio.

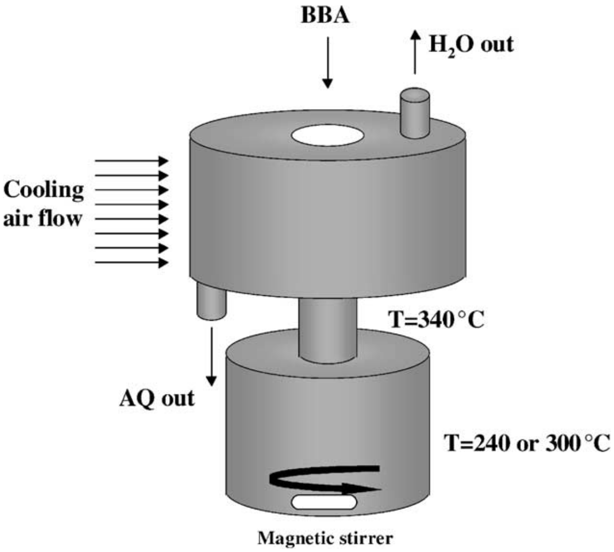

Fig. 1. Scheme of the reactor/evaporator employed in the pseudo-continuous runs.

3. Results and discussion

The results of the screening of different heteropolyacid solid catalysts are reported in Table 1 for comparison with previous results [1] on zeolites, bentonites and other solid catalysts.

All the tested polyoxometalate catalysts show good yields in AQ with respect to other solid acid materials considering the fact that the former are employed in a typical catalytic ratio to the reactant (1:1000 molar ratio), while the latter are introduced in a much larger amount (1:2 in weight).

On the basis of this preliminary screening, the behaviour of the catalyst $H_7PW_{12}O_{42}\cdot xH_2O$, that performed the best in terms of AQ yields, has been studied in the pseudo-continuous reactor. The operative conditions chosen consist, in this case, in a molar ratio of BBA to catalyst of 100 (or BBA:H^+ of 33). This catalyst has been synthesised according to the procedure proposed by Bailar [15] and is reported in the paper with such formula; that is the acid has been considered as heptabasic although other authors suggested alternative formulas, as mentioned in the same paper.

Two experimental runs have been performed, at 240 °C and at 300 °C by introducing in the reactor an initial quantity of BBA of 7 g. The AQ produced evaporates and is collected at intervals of about 60 min. The bright yellow crystalline product had a purity of more than 99%. During the run, collected AQ is weighed and a corresponding molar amount of BBA is fed to the reactor.

In Figs. 3 and 5 the overall productivity of AQ is reported as a function of time for respectively the runs at 240 and 300 °C. Overall productivity is the amount of pure AQ collected at the top of the reactor referred to the unit of time and mass of catalyst. The same results are reported in Figs. 2 and 4 in terms of the total amount of AQ collected at the top of the reactor as a function of time. Some scattering in the experimental data is evident in these figures; this has been attributed to the manual operation of withdrawing solid product and feeding reagent involving a temporary disconnection of the reactor oven.

The activity and productivity of the polyoxometalates, are higher than the ones observed on other solid acid catalysts, such as zeolites, as it can be appreciated in a previous work [1], also in pseudo-continuous longer runs. In particular the run performed at 300 °C shows a productivity that is more than one order of magnitude higher. Moreover, it is useful to emphasise that the polyoxometalates show a limited trend to deactivation during time opposite to what observed for the other catalysts [1].

4. Kinetic model

The runs reported in Figs. 2–5 have been correlated by using a kinetic model with vapour–liquid partition [1] that considers reaction (2) written in the following

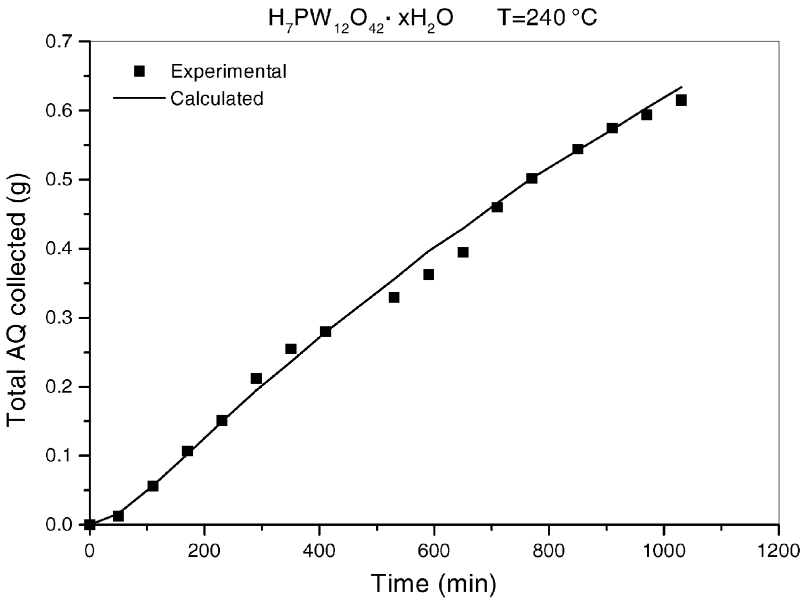

Fig. 2. Total AQ collected vs. time for the run at 240 °C.

schematic form

$$BBA \rightarrow AQ + H_2O \quad (3)$$

The evolution with time of the reactant and products can be expressed by the following equation

$$-\frac{dn_{BBA}}{dt} = \frac{dn_{AQ}}{dt} = \frac{dn_{H_2O}}{dt} = r \quad (4)$$

For the reaction rate, r, we have assumed a zero-order kinetics that fits slightly better than the first order one with the experimental data. The real reaction order is probably intermediate between 0 and 1 corresponding to a Langmuir–Hinshelwood kinetic model. For the zero-order kinetics the rate equation is

$$r = k_c m \quad (5)$$

By taking into account that, although small, a deactivation of the catalyst occurs we have introduced a deactivation law of the type

$$k_c = \frac{k_0}{1 + k_d t} \quad (6)$$

For vapour–liquid partition we assume that all the water formed evaporates in the atmosphere, while, AQ is

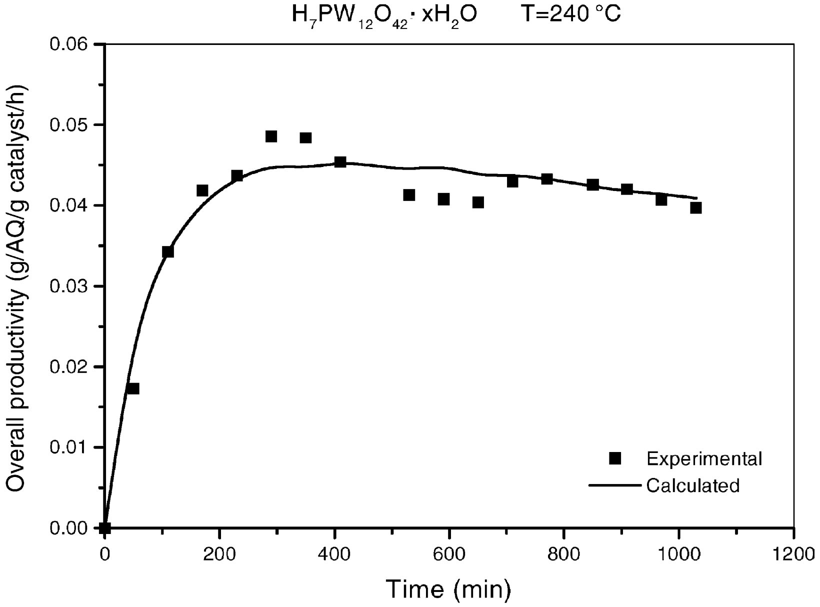

Fig. 3. Overall productivity in AQ for the run at 240 °C.

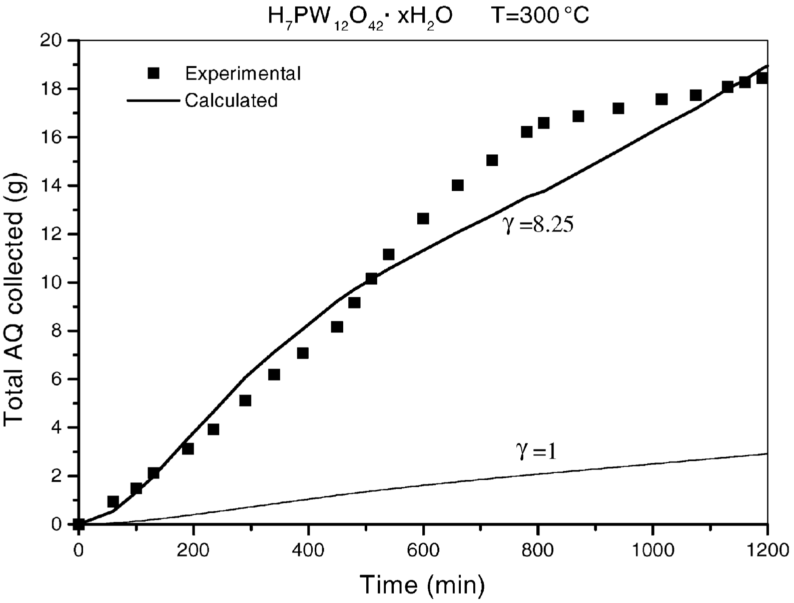

Fig. 4. Total AQ collected vs. time for the run at 300 °C. Comparison is reported between model simulation assuming ideal liquid mixture ($\gamma = 1$) and a simulation with a non-ideal behaviour ($\gamma = 8.25$).

partitioned between liquid and vapour phase and then the accumulation of this product in the liquid phase can be described by

$$\frac{dn_{AQ}^{L}}{dt} = r - Jy_{AQ} \tag{7}$$

where J is the total vapour flow-rate expressed by the sum of two terms related to AQ and water

$$J = J_{AQ} + J_{H_2O} = J_{AQ} + r \tag{8}$$

Introducing the vapour–liquid relation relative to AQ, we can write

$$Py_{AQ} = \gamma_{AQ} x_{AQ} P_{AQ}^{0} \tag{9}$$

Then, at a total pressure $P = 1$ atm and combining the relations (8) and (9) we obtain an expression for the mole fraction of AQ in the vapour phase

$$y_{AQ} = \gamma_{AQ} x_{AQ} P_{AQ}^{0} = \frac{J_{AQ}}{J_{AQ} + r} \tag{10}$$

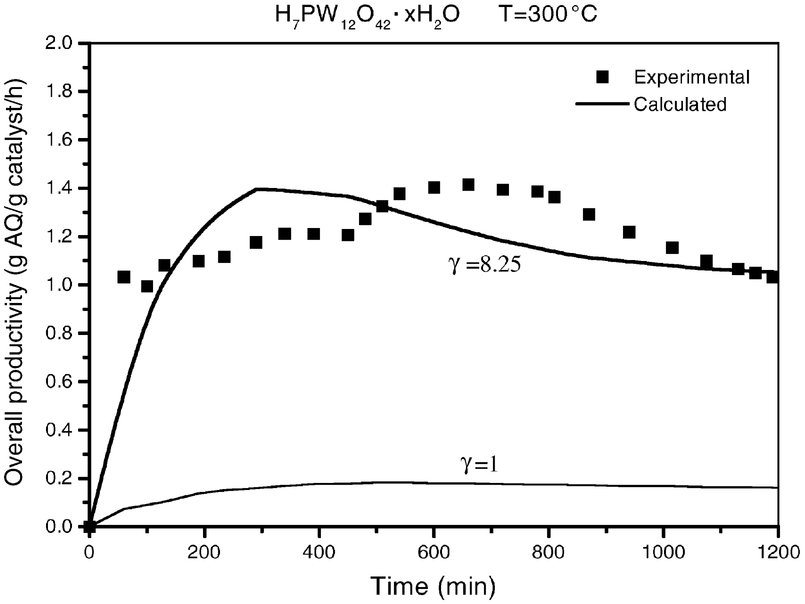

Fig. 5. Overall productivity in AQ for the run at 300 °C. Comparison is reported between model simulation assuming ideal liquid mixture ($\gamma = 1$) and a simulation with a non-ideal behaviour ($\gamma = 8.25$).

Table 3
Parameters used in the model

Pseudo-continuous run (°C)	k_0 (mol min^{-1} g^{-1} catalyst)	k_d (min^{-1})	γ_{AQ}
240	0.1419×10^{-3}	0.9633×10^{-3}	8.75
300	0.1702×10^{-3}	0.1712×10^{-2}	8.25

The obtained expression (10) can be introduced in the balance Eq. (7) to give

$$\frac{dn^L_{AQ}}{dt} = r\left[1-\left(1+\frac{\gamma_{AQ}x_{AQ}P^0_{AQ}}{1-\gamma_{AQ}x_{AQ}P^0_{AQ}}\right)\gamma_{AQ}x_{AQ}P^0_{AQ}\right] \qquad (11)$$

The integration of this ordinary differential equation, coupled with relation (4), can be performed by taking into account the overall material balance on AQ expressed by

$$n^S_{AQ} = n^0_{BBA} - n_{BBA} - n^L_{AQ} \qquad (12)$$

and the following initial conditions

$$\text{at } t = 0 : n_{BBA} = n^0_{BBA};\ n^L_{AQ} = 0;\ n^S_{AQ} = 0;\ n_{AQ} = 0 \qquad (13)$$

All the runs performed have been simulated and the agreement between the experimental data and the model is shown in Figs. 3 and 5, for the overall productivity, and in Figs. 2 and 4 for the amount of AQ collected versus the time. Table 3

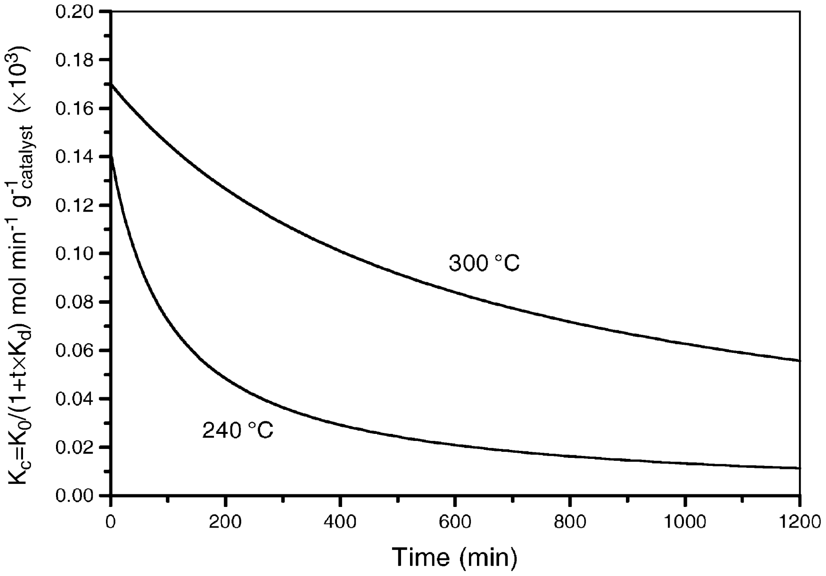

Fig. 6. Deactivation law for the kinetic constant relative to the two pseudo-continuous runs.

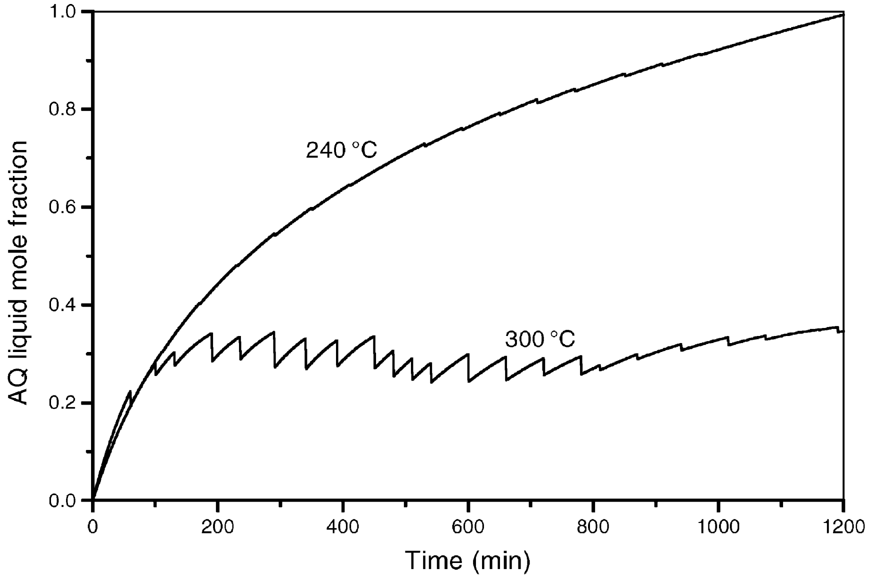

Fig. 7. AQ accumulation in the liquid phase as a function of time.

lists the parameters estimated by non-linear regression on the experimental data.

It appears that assuming an ideal behaviour of the liquid phase ($\gamma_{AQ} = 1$) and on the basis of the vapour pressure of AQ [14] the experimental observations in terms of collected AQ and of the final composition of the liquid phase cannot be reproduced (see Figs. 4 and 5). To account for such large deviation from ideality, to which can be ascribed the active evaporation of AQ, we have determined an activity coefficient for each run by a trial-and-error procedure and selecting the value that allow the description of both the solid AQ collected amount and the final composition of the liquid phase, that is, $X_{AQ} = 0.35$ for the run at 300 °C and $X_{AQ} \cong 0.9$ for the run at 240 °C.

The trend of the kinetic constant with time according to the deactivation law represented by relation (6) is given for the two runs at different temperature in Fig. 6.

Fig. 7 shows the evolution with time of the amount of AQ accumulated in the liquid phase, as estimated by the model for the two performed pseudo-continuous runs. The marked difference in the behaviour between the two explored temperatures, can be ascribed to the low volatility of AQ at 240 °C leading to accumulation of AQ in the liquid phase during practically the whole run. In contrast, at 300 °C, AQ is easily transferred to the vapour phase resulting in pseudo-stationary conditions after about 200 min from the start of the run.

5. Conclusions

The cyclization of BBA is catalysed by solid acid polyoxametalates which show an activity that is much higher than that previously observed for other solid acid catalysts such as bentonites and zeolites.

The multifunctional reactor employed allows to collect productivity data for the considered solid catalysts and a direct comparison between them has been performed. A kinetic model with non-ideal vapour–liquid partition and catalyst deactivation has been employed to describe the behaviour of the pseudo-continuous runs. The high activity coefficient of AQ allows the recovery of this product by evaporation at relatively low temperatures.

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